

LI.—*An Explanation of the Property of Induced Polarity of Atoms and an Interpretation of the Theory of Partial Valencies on an Electronic Basis.*

By WILLIAM OGILVY KERMACK and ROBERT ROBINSON.

IN recent times it has become more and more evident that the graphical formulæ employed by organic chemists to represent the constitutions of chemical individuals are expressions which inadequately symbolise the properties of substances, and from time to time efforts have been made to introduce additional systems of notation corresponding with more or less definite theoretical ideas. Thus the sign adopted by Thiele to denote the existence of conjugation of ethylene linking involves the theory of residual affinity which is almost but not quite identical with that of partial valencies of definite alternately positive and negative polarity as formulated by one of us in order to develop a more convenient representation of the ethylene-nitrogen conjugated system. This theory of partial

valencies equivalent in the sum to the normal valencies from which they are derived has also been applied to the explanation of intramolecular transpositions and of the nature of aromatic homocyclic and heterocyclic types. Similarly, Flürscheim developed a system of exhibiting the now well-recognised alternate effect in chains of atoms by means of thick and thin lines showing augmented and diminished affinities, and Vorländer has used + and - signs with almost the same implication. Michael was perhaps the most important pioneer in emphasising the importance of the influence of the electrical polarity of atoms and groups in molecules, and Lapworth's theory of induced latent polarity of atoms, which, starting from a key-atom of recognised polarity, are alternately positive and negative in a chain, combines and extends the views of Flürscheim and of Michael and has proved extremely useful in collating the data accumulated in connexion with such problems as orientation and the mechanism of reactions. Again, Werner has found it necessary to introduce modifications in the conventional representation of the nature of "onium" salts and of "complex" or co-ordinated compounds generally, and the application of his methods has been extended with striking success to many related types, for example, the triphenylmethane and azine dyes and oxonium salts of the anhydropyranol or pyrylium class. Finally, the behaviour of the now numerous isolated radicles such as triphenylmethyl is not well expressed by formulæ with a normal free valency bond, and some kind of partial saturation of the latter by the unsaturated atoms which occur in the molecules of all these substances has frequently been postulated.

Whilst all these theories and their corresponding devices of symbolisation have proved serviceable as working hypotheses, the connecting link in the form of a common physical basis is lacking, and it is the object of the present communication to suggest that such may be found in the Thomson and Lewis-Langmuir theory \*

\* The suggestions of Abegg and Bodländer (*Z. anorg. Chem.*, 1899, **20**, 453) and of Abegg (*ibid.*, 1904, **39**, 330) should undoubtedly be mentioned as clearing the ground for the later recognition of the stability of the electron octet, but in the development of modern electronic views of the nature of valency by far the most influential worker has been Sir Joseph Thomson (Silliman Lectures, "Electricity and Matter," 1903: *Phil. Mag.*, 1904, [vi], **7**, 237; 1906, [vi], **11**, 769; 1921, [vi], **41**, 510), whose theory of the nature of the chemical bond comprises all the features which are really essential to the interpretation of the symbols employed by organic chemists. The benzene formula given on p. 437 has already been put forward by Thomson. Ramsay expressed the electrical view of chemical combination in a form particularly adapted to appeal to chemists (T., 1908, **93**, 778), and in connexion with the possibility that one electron may be shared by more than two atoms (and vice versa) (see p. 433), Lodge (*Nature*, 1904, **70**, 176) has made sugges-

of the atom and of valency which we employ in the simplified form in which it was expounded by Langmuir at the Edinburgh meeting (1921) of the British Association for the Advancement of Science.

### 1. *General.*

The outstanding feature of Langmuir's theory which is adopted in the sequel is the explanation of the nature of chemical combination and the recognition of the tendency to form stable octets of electrons in the case of those elements (except hydrogen) which most commonly occur in carbon compounds. With Langmuir, we take a single bond to mean the sharing of two electrons by the atoms connected and a double bond the sharing of four. We desire, however, to suggest that the facts of organic chemistry are best interpreted if it be assumed in addition that it is possible for contiguous atoms to share one or three electrons. In the case of a triple bond, it is thought that the sharing of six electrons, although possible, represents an unstable condition, and the tendency will be for one of the atoms (carbon or nitrogen) to complete its octet in a more stable configuration. It may be recalled that Langmuir has already suggested the deformation of the octet in order to preserve the tetrahedral environment of the carbon atom, and in our view it is the number of electrons, and not a precise definition of their supposed arrangement in space, which is of vital significance.

### 2. *Co-valence and Electro-valence.*

It would seem that a sharp distinction between these two types of valency is not possible, and our views on this subject are precisely those which have already been clearly expressed by Briggs (T., 1921,

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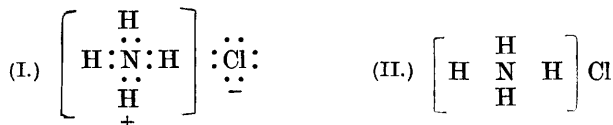
tions which are so relevant to the subject of the nature of partial valency that two sentences may be quoted:—

“On any view electrons are supposed to repel and be attracted with a force varying as the inverse square of the distance, and this is only consistent with a very large number of lines of force radiating from each and starting out in every direction equally.”

“When opposite charges have paired off in solitude, every one of these lines starts from one and terminates on the other constituent of the pair, and the bundle or field of lines constitutes a full chemical bond; but bring other charges or other pairs in the neighbourhood, and a few threads or feelers are at once available for partial adhesion in cross directions also.”

The following references to the papers of Lewis and of Langmuir may be given: G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; I. Langmuir, *Proc. Nat. Acad. Sci.*, 1919, **5**, 252; *J. Amer. Chem. Soc.*, 1919, **41**, 868, 1543; 1920, **42**, 274; *Science*, 1920, **51**, 605. Compare also W. Kossel, *Z. Physik*, 1920, **1**, 395.

119, 1879). It is obvious that the Thomson and Lewis-Langmuir theory (I) of the nature of ammonium chloride is precisely that which Werner developed on purely chemical grounds (II).



No difficulties are experienced in applying similar expressions to complex quaternary ammonium salts such as the canadine metho-salts, whereas such formulæ as  $\text{NH}_3 \cdots \text{HCl}$  lead to anomalies.

### 3. Polar Character of Atoms in Combination.

An atom is called negative which is surrounded by a stable octet or which tends to attract electrons so as to make up a stable octet. The octets are the more stable the less the electrons are restrained by being shared with other atoms and also the smaller the atomic weight of the element. The tendency to form an octet is the greater the more nearly it is already formed. Conversely, a dis-integrated octet tends to further disruption, and atoms surrounded by such unstable systems tend to lose electrons and are positive in polar character. The positive nature of hydrogen implies that a stable condition is reached when no electrons surround the nucleus.

Independent of the considerations discussed below, it seems certain that the introduction of electronegative atoms, such as O, N, Cl, in any position in a molecule increases the power of the whole assemblage to retain electrons. There may still be relative intramolecular differentiations of polarity, but the entire electro-negative tone will be raised. An example of this effect is the increased dissociation constant of acids following on the replacement of hydrogen by halogen. The converse proposition holds. The carbon atom is assumed to be nearly neutral in saturated compounds, but its condition in most cases represents a state of compromise, and the arrangement surrounding it is peculiarly susceptible to external influences. Unsaturated carbon atoms may be either negative or positive, according to circumstances.

In the absence of powerful external influences, the following rules appear to afford a trustworthy guide as to the polarity exhibited by carbon atoms in various states of combination. The attachment of carbon to carbon by two electrons induces a very slight constraint on the two octets of which they form a part. This is progressively increased when the number of shared electrons is three and four, and a decided positive polarity of unsaturated carbon is the outcome.

This accounts for the increased mobility of electrons in unsaturated compounds and naturally as a corollary for the selective absorption of light. External influences are, however, seldom absent, and in their presence the function of an unsaturated system, particularly the benzene ring, seems to be analogous to that of a resonator. That is, the external group itself helps to set up a position in which the actual polarity of unsaturated carbon appears to be negative. This is easy to appreciate where a group X affects a group Y via a benzene ring, but what we are now suggesting is that in some cases X affects its own reactivity by the mere fact that it occupies a certain position relative to an unsaturated system.

#### 4. *Induced Polarity in a Chain of Atoms.*

It is possible to represent the majority of carbon compounds so as to have an octet surrounding each carbon, nitrogen, or oxygen atom, but it is quite clear that these cannot all be of equal stability, unless indeed the substance is symmetrically constituted. If in the system,  $\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{A}}}\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{B}}}\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{C}}}\text{:}\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{D}}}\text{:}$ , for some reason internal or external the octet surrounding A becomes stable, this will automatically involve more or less appropriation of the two electrons shared with B, the octet surrounding which is therefore unstable and tends to disintegrate. If, now, another atom C is attached to B, it will have no difficulty in appropriating two further electrons from B, and in doing so may form a stable octet. This again will preclude a fourth member of the chain D from forming a stable octet. In other words, the atoms A, B, C, and D are respectively,  $-$ ,  $+$ ,  $-$ ,  $+$ . The case of allyl chloride may be cited as a simple example :

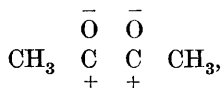


Here the stable octet surrounding the chlorine atom produces an unstable system about the adjacent carbon atom, and therefore the formation of a stable system in the CH group is facilitated and occurs by the aid of two of the electrons held in common with the second unsaturated carbon atom. It is accordingly quite natural that the product of the addition of  $\overset{+}{\text{H}} \overset{-}{\text{Br}}$  is trimethylene chlorobromide,  $\text{Cl}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ .

The case of the influence of positive atoms such as hydrogen and the alkali metals may be considered on precisely similar lines. Such atoms tend to give up an electron and in this way tend to assist the adjacent atom to form a stable octet, and the alternate stable

and unstable systems involving alternate negative and positive polarity are again set up. It must be clearly understood that this view refers only to the mechanism of the alternate effect, and not to the circumstances which induce the "key"-atom to assume its stable octet or to lose an electron. For it is probable that in many molecules the electrons are in a delicate condition of equilibrium very susceptible to external influences, and the character of these may virtually determine the orientation of the alternating stable octets. In the molecules of some substances, however, the activation of any one of the possible "key"-atoms would produce identical results, and in such cases it is certainly feasible to write polar formulæ which will express the behaviour of the compounds in all circumstances. Examples may be found in the structures of *tert.*-butyl alcohol, acetone, acetic acid, acetonitrile, acetoacetic acid, acetonedicarboxylic acid, phloroglucinol in either tautomeric form, orcinol, mesitylene, *s*-xylidine, and many other compounds. One further advantage of the Thomson and Lewis-Langmuir theory in relation to this subject may be noted. Experience has shown that the alternating effect is transmitted but feebly by saturated atoms, whereas it may be discerned at the end of long chains wholly comprised of unsaturated atoms. This is easy to understand in view of the fact that unsaturated atoms share more electrons in common than saturated atoms. There will be a greater mobility of electrons, and the octets, when formed, will have some units at least which are not subject to restraint, a condition which tends to stability.

Although stable octets associated with alternate atoms in a chain represent what is apparently the most common arrangement, it is probable that other structures also occur. For example, in the case of  $\alpha$ -diketones such as dimethyl diketone we may write:—



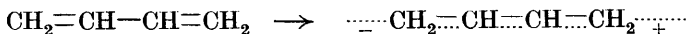
and this formulation harmonises with the ready oxidation of the compound by hydrogen peroxide with formation of acetic acid. The quinones are in a similar class, and if these substances are at least partly peroxidic, the explanation may be the tendency to change from the abnormal to the normal (alternate) arrangement of relatively stable octets.

### 5. Primary Conjugation.

The term "primary conjugation" is used to denote a process occurring in the course of a reaction resulting in addition to the

terminal members of an unsaturated system of more than two atoms.

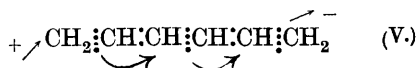
(a) *Conjugation of Ethylene Linkings.*—The representation of the active phase and conjugation of butadiene on the partial valency theory is



and on the Thomson and Lewis-Langmuir theory as now interpreted



Similarly, the conjugation of three double bonds, supposing such to occur, would be represented thus:—



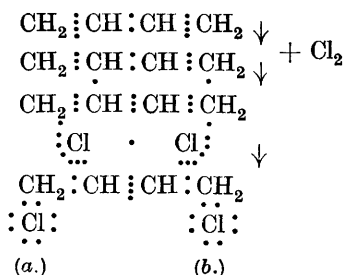
Therefore the notation which has been used in the development of the theory of partial valency acquires a physical meaning if we assume that the symbols  $\equiv$ ,  $\cdots$ ,  $-$ ,  $\cdots$  imply electrons to the number of four, three, two, and one, respectively, held in common by two atoms. Subdivision of a normal valency into more than two partial valencies is accordingly a proceeding of doubtful validity unless one electron can be shared by more than two atoms, or one positive charge on an atomic nucleus by more than two electrons. There is nothing improbable in such an assumption, since the division of the tube or bundle of tubes of force emanating from an electron is already assumed in the hypothesis of shared electrons. Returning to the question of conjugation, we may now consider the mechanism of the additive process. The polarised complexes (IV, V) represent an extreme and highly unstable condition which cannot be the normal state. More stable molecules are the open-chain, non-polarised (III), and the cyclic forms, which latter in the case of butadiene is shown in VI and VII, electronic and partial valency formulæ respectively.



Now either in III or VI the system is probably an oscillating one, the terminal carbon atoms becoming in turn feebly electropositive and electronegative,\* and in the absence of a reagent this is the

\* In the case of unsymmetrical substances, the considerations discussed in section (4) will determine the polarity of the unsaturated atoms.

extent of the conjugation. We suppose, however, that the reactant takes advantage of these momentary manifestations of polarity and that the process is then carried forward as illustrated below or in some such manner.

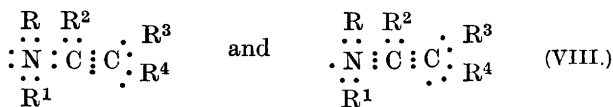


In words, the electrons joining the chlorine atoms one at a time attack a terminal unsaturated carbon atom, driving an electron from the other terminal carbon atom into the electron system surrounding one of the chlorine atoms (b). There may, of course, be several intermediate phases, but any such modifications do not affect the principle.

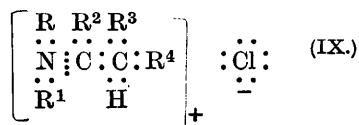
(b) *The Ethylene-Nitrogen Conjugated System.*—The partial valency representation of the polarised form of a base,



and the corresponding expressions on the basis of the electronic theory are



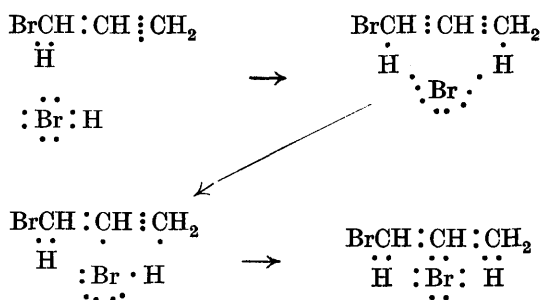
It is clear the expression VIII denotes a mere alteration in function of the electrons composing the octets, and one of the salt-forming electrons on nitrogen becomes shared with the next carbon, a free electron appearing on the terminal unsaturated carbon atom of the system. If this process occurs a second time, probably as the result of the approach of a reactive molecule capable of dissociation, it may be the carbon which attracts the positive component, and with hydrogen chloride we get the salt (IX).



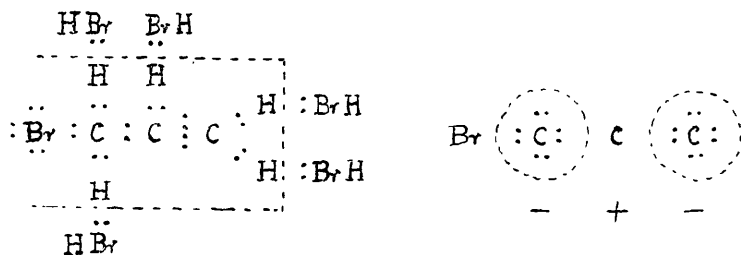




result of the activation of a "key"-atom in a molecule on the approach of other molecules either of solvent or reagent. The best examples are to be found in the reactions of aromatic compounds, but in order to illustrate our meaning the addition of hydrobromic acid to allyl bromide may be cited, since this is one of the simplest cases of a reaction proceeding in two directions. The product may be either trimethylene dibromide or propylene dibromide, and, in the former case, a secondary conjugation may be involved, or, on the other hand, it may not, since the normal arrangement in allyl bromide will probably be similar to that given above for allyl chloride and trimethylene dibromide is the natural product. The formation of propylene dibromide is, however, abnormal and the result of the secondary conjugation illustrated below:—



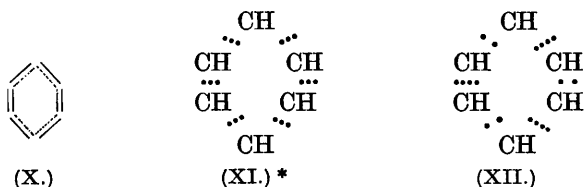
This idea of a loose union between the hydrogen atom and the bromine resulting in orientation of the additive reaction can also be expressed in another way, as shown in the annexed scheme, which represents a process bearing some analogy with Baly's activation of molecules by opening up their fields of force (*Physikal. Z.*, 1913, 14, 893):



The loosening of the hydrogen atoms by the bromine produces the result illustrated alongside on the stability of the octets. It should be noted that the effect of the centrally situated hydrogen atom opposes that of the remaining four.

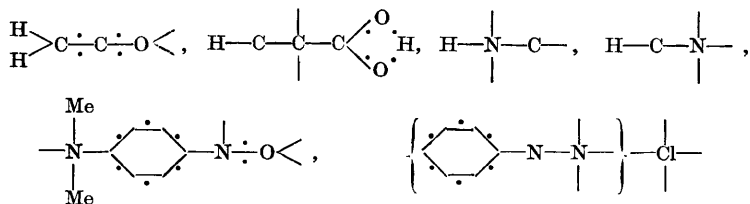
7. *Aromatic Nuclei.*

(a) *Homocyclic Types.*—In discussing the subject of conjugation, we have tacitly assumed that three electrons shared by two atoms is a relatively stable configuration, and the electronic formula for benzene corresponding with the cyclic conjugated expression with six sesquivalencies (X) is shown in XI.

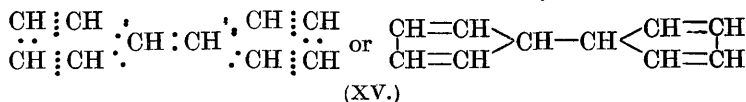


The relation of XI to the Kekulé formula XII is seen to be a remarkably close one and to involve the movements of electrons, not from atom to atom, but merely to new positions in three octets. If, therefore, the benzene molecule is in fact, as many chemists have assumed, subject to vibrations and in a dynamic condition, a relatively insignificant rearrangement is required in order to pass from one Kekulé formula to the other. This consideration suffices to explain the non-existence of pentamethine (XIII) or any of its derivatives, since this compound could scarcely survive the passage into the phase XIV without undergoing polymerisation to a substance such as XV.

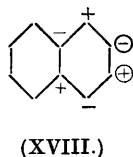
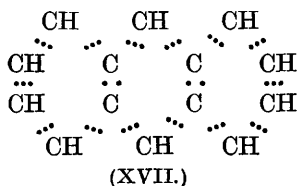
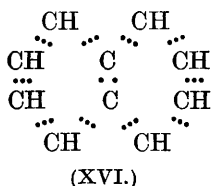
\* We venture to suggest that the following conventional notation is simple and convenient. Represent a single electron by a dot (and if held in common by two atoms its position will indicate this), two electrons by an ordinary bond. Varied structures are readily expressed in this manner; thus our view of the electronic constitutions of keten, propiolic acid, carbylamine, formonitrile, nitrosodimethylaniline, and benzenediazonium chloride are the following :—



The formula chosen for the carboxyl group is identical with the expression,  $\text{—C} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{H}$ , recommended by Hantzsch and by Lapworth.



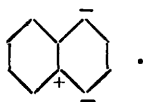
The most stable or mean phases of naphthalene and anthracene are shown in (XVI) and (XVII) respectively,



and it is interesting to observe that whatever arrangement of octets is chosen it is impossible that both the central quaternary atoms in naphthalene or more than two such atoms in anthracene can be surrounded by stable electron systems. One of these atoms in naphthalene and two of them in anthracene \* must therefore be intensely positive, and, in accordance with the considerations advanced in (4) above, this explains very satisfactorily the reactive nature of the  $\alpha$ -position in naphthalene and the 9- and 10-positions in anthracene. Taking the case of naphthalene, we have the

\* As a matter of fact, the environment of the central carbon atoms of the naphthalene and anthracene nuclei tends to make them all positive, in accordance with the views expressed on p. 430 in connexion with the effect of various types of combination on the polarity of carbon atoms. The suggestion put forward in the text implies that in the case of one of these atoms in naphthalene the tendency to form a system of alternate stable and unstable octets overbears its natural positive character. This again is bound up with the nature of the mechanism of substitution in aromatic compounds, the theory adopted being correlated with the additive hypothesis of such reactions. In considering the chemistry of polynuclear compounds generally, it should, however, be remembered that the carbon atoms common to two rings have a tendency to evince positive polar character.

The possibility must not be overlooked that the types represented by  $\text{H}_2$ ,  $\text{Br}_2$ , and  $\text{HO}\cdot\text{NO}_2$  may react most easily with different phases of an unsaturated molecule. Thus the formation of 1:4-dihydronaphthalene appears natural if regarded as the result of a symmetrical addition of hydrogen to naphthalene in the phase



condition shown in XVIII, and addition occurs to the 1 : 4-positions preferentially as being the nearest to the source of the disturbance leading in non-reversible substitutions to the replacement of hydrogen in the  $\alpha$ -position. In reversible substitutions, for example, sulphonation, the weaker induced activity of the  $\beta$ -positions can come into operation.

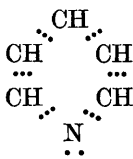
(b) *Heterocyclic Types*.—The heterocyclic aromatic substances which are typical of all others are pyridine and pyrrole, and to these the cyclic conjugated formulæ XIX and XX have been assigned by one of us in order to express the basic properties of the former substance and the non-basic properties of the latter.



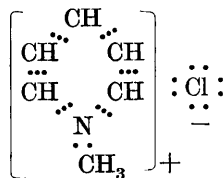
(XIX.)



(XX.)

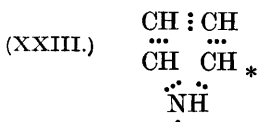


(XXI.)

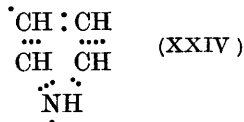


(XXII.)

The case of pyridine presents no unusual feature, and the formulæ XXI and XXII can be assigned to the base and its methochloride. Pyrrole, however, appears to have a peculiar electronic configuration, shown in XXIII, which is an exact rendering of XX in accordance with the principles suggested above in discussing the ethylene-



(XXIII.)



(XXIV.)

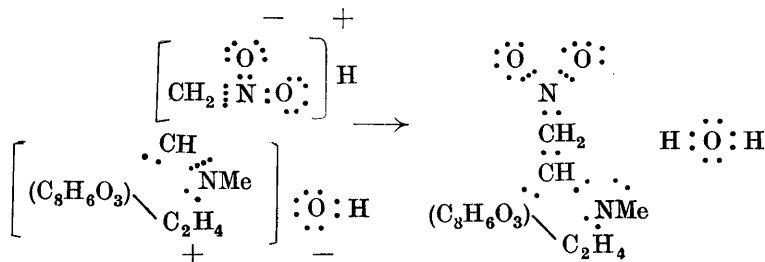
nitrogen conjugated system. The peculiarity is the existence of an unrestrained electron, denoted by an asterisk, on the  $\alpha$ -carbon atom. The properties of pyrrole are in complete harmony with this interpretation.

The occasional reactivity of the  $\beta$ -position is due to incomplete conjugation resulting in the phase XXIV, and on the basis of these views it is readily explicable that it is the  $\alpha$ -position which is the most reactive in pyrrole and the  $\beta$ -position in indole.

### 8. Mechanism of Reactions.

The mechanism of reactions appears in many cases notably simplified by a reference to the electronic basis. As a single example we take the condensation of a pseudo-acid (nitromethane) in its *aci*-form with a pseudo-base (cotarnine) in its ammonium hydroxide

form, leading to a product (anhydrocotarninenitromethane), in which both acid and base automatically revert to the pseudo-condition.



The only rearrangements of electrons involved in this process are in the octets themselves and in no case does an electron leave the octet of which it forms a part.

Finally, it may be noted that intramolecular rearrangements are equally readily represented, and that, for example, the generalised form (R. Robinson, *Mem. Manchester Phil. Soc.*, 1920, 64, iv, 7) of the pinacone-pinacolin and Wagner transformations is capable of literal translation into the electronic expressions if to the partial valencies is given the meaning suggested on p. 433.

In the foregoing, an attempt has been made to show that the Thomson and Lewis-Langmuir theory of valency and electron configuration furnishes a satisfactory physical basis for certain modern hypotheses of organic chemistry, and if this attempt has been at all successful the matter is certainly not lacking in that special interest which accrues when ideas derived from different points of view are found to be compatible.

A very brief statement of these views was sent to Professor A. Lapworth, F.R.S., in December, 1921, and he at once replied that he had drawn similar conclusions which were embodied in a general form in a paper which he had submitted to the Society a short time before the receipt of the letter. The present communication is the outcome of his generous suggestion that we should submit our manuscript before having an opportunity to consult his own publication.

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